Measurement of atmospheric chlorides

Foran, M. R.

Internal Report (National Research Council of Canada. Division of Building Research), 1960-11-01

NATIONAL RESEARCH COUNCIL

CANADA

DIVISION OF BUILDING RESEARCH

THE MEASUREMENT OF ATMOSPHERIC CHLORIDES

by

M. R. Foran

Internal Report No. 214

of the

Division of Building Research

OTTAWA

November 1960

Preface

It is now known that results from studies of corrosion of metal specimens set out at outdoor exposure sites are difficult to interpret unless corresponding measurements can be made of the local variations in the factors which may cause corrosion rates to differ from site to site and with time. Techniques have been available for measurement of sulphur dioxide levels, and the Division has regularly made such determinations at the eight exposure sites which it maintains across Canada. More recently instrumentation has been developed for the determination of time of wetness. Atmospheric chlorides have long been thought to be important in influencing corrosion rates but techniques suitable for their measurement at corrosion sites have not been available. The proposal from the Nova Scotia Research Foundation to investigate possible techniques was therefore welcomed. The literature survey and field experiments carried out in 1955-56 were recorded in DBR Report No. 122. The second report on this work is now presented. The author, Dr. M. R. Foran is Professor of Chemical Engineering at Nova Scotia Technical College.

Ottawa
November 1960

N. B. Hutcheon
Assistant Director

The Measurement of Atmospheric Chlorides

by

M. R. Foran

In the Spring of 1956 the Nova Scotia Research Foundation arranged with the Division of Building Research of the National Research Council to have a summer research student investigate some of the methods which might be used to determine the salt content of the air at corrosion sites where no electrical power was available and where there was no continuous supervision.

A survey of the literature did not reveal any conclusive fact about the size of the salt particle which must be measured in order to relate the corrosion of metals to the salt content of the air. A general discussion of the various methods can be found in Internal Report No. 122 of the Division of Building Research.

The results presented in this report are those obtained by the "Wet Candle" and the "Rainfall Can" methods, which are described.

Wet Candle Method

The wet candles were prepared by wrapping three strips of No. 2 gauze bandage about 28 in. long, folded along its length around that portion of an inverted $5\frac{3}{4}$-in. test tube protruding above a rubber stopper which closed a 500-ml wide-mouth flask or a 16-oz polyethylene bottle. Any chloride in the gauze had been removed previously by boiling in distilled water. The ends of the gauze dipped into a 20 per cent

glycerine solution which prevented excessive evaporation, but not expansion, during severe freezing.

Rainfall Can Method

The rainwater was collected in 2.5-gal. blue polyethylene containers fitted with 6-in. diameter cylinders which projected upwards. These were used because the standard black rainfall cylinders were not available when the tests were begun. Three containers were securely fixed about one foot apart on a wooden plank. The exposure arrangement at York Redoubt is shown in Fig. 1.

The data were collected over the period, August 1958 to April 1960. Two sites were chosen: York Redoubt, about 7 miles from Halifax and considered rural; and the roof of the Macdonald Building at Nova Scotia Technical College, an urban location. Results are an average of determinations on three wet candles and three rainfall cans at each site.

Data collected at these sites and others have been reported previously by Foran, Gibbons and Wellington (1).

Object

The object of this report is a) to present the results collected at the two sites mentioned above; and b) to compare the results obtained by the rainfall can and wet candle methods in order to find a possible correlation.

Analytical Methods

The liquid contents of each wet candle flask are transferred to a one litre beaker. The gauze is removed

separately and placed in a 600 ml beaker and its chloride content is removed by leaching three times with boiling distilled water. The leached chloride obtained in this way is added to the main solution. The test tube and container are also rinsed thoroughly with hot water, and the rinse water added to the main solution.

The main solution is then concentrated by evaporation to a volume of 200 ml. The solution is then filtered, and the hot filtrate is treated with 5 ml permanganate solution to oxidize impurities. The solution is heated further until the brown precipitate of hydrated manganese dioxide coagulates and is filtered to remove the precipitate.

The filtrate so obtained should be clear and have a volume of about 250 ml. Any yellow colour present may have been the result of decomposition of the glycerine due to excessive heating and/or concentration of the solution during evaporation. Such colour may be removed by the addition of 0.5 gm of activated charcoal (chloride free) followed by stirring and filtering. A blank solution should be prepared by mixing 70 ml glycerine with 180 ml water.

The chloride contents of both sample and blank are determined by the Mohr method, using a dilute solution of silver nitrate as titrant. (One ml of $AgNO_3$ should be equivalent to about 1 mg NaCl.)

Ten millilitres of a 5 per cent solution of potassium chromate, K_2CrO_4, are used as indicator for each sample. The silver nitrate is preferably added from a 10 ml burette, calibrated to $\pm$ 0.05 ml. In titrating the blank solution,

care is exercised to ensure that the same colour is obtained at the end point as for the sample. The blank reading is deducted from the amount of $AgNO_3$ required for each sample, and the weights of sodium chloride are then calculated from the corrected quantities of the $AgNO_3$ solution required.

The rainfall cans were rinsed with distilled water, the water evaporated to 250 ml and the titrations carried out in the manner outlined above.

Results

The results of the tests are shown in Tables I and II and Figs. Nos. 2, 3, 4, 5, 6, 7.

In Figs. 2 and 3 the results obtained by the rainfall can and wet candle methods along with the total precipitation as reported by the Halifax Weather Office, of the Meteorological Service of Canada, are plotted against the months of the year. In Figs. 4 and 5 the readings obtained by the wet candle method are plotted against those from the rainfall can method for each site.

TABLE I

ATMOSPHERIC CHLORIDE AT YORK REDOUBT

Year	Month	Rainfall Cans (mg NaCl/metre^2 day)	Wet Candles (mg NaCl/metre^2 day)
1958	August	8.02	13.0
	September	23.94	48.0
	October	12.09	26.0
	November	30.36	57.0
	December	24.52	-
1959	January	24.30	57.0
	February	10.51	68.0
	March	85.77	100.00
	April	11.79	38.0
	May	-	14.0
	June	30.63	21.40
	July	13.96	17.16
	August	4.69	6.86
	September	-	15.75
	October	-	51.19
	November	-	71.47
	December	-	30.95
1960	January	-	26.58
	February	-	60.01
	March	-	15.59
	April	-	26.76

TABLE II

ATMOSPHERIC CHLORIDE AT THE NOVA SCOTIA TECHNICAL COLLEGE

Year	Month	Rainfall Cans (mg NaCl/metre^2 day)	Wet Candles (mg NaCl/metre^2 day)
1958	August	8.0	16.0
	September	18.3	41.0
	October	16.9	29.0
	November	17.2	32.0
	December	16.5	32.0
1959	January	20.1	31.0
	February	16.0	32.0
	March	76.3	11.1
	April	74.2	35.0
	May	25.3	34.0
	June	41.6	29.9
	July	27.5	20.0

Discussion

The plot of rainfall can readings against wet candle results at York Redoubt (Fig. 4) seems to indicate a definite correlation. The line shown was calculated by the method of least squares and its equation was found to be

$$Y = 1.02 x + 16.0$$

where

Y = wet candle reading (mg NaCl/metre^2 day)

x = rainfall can reading (mg NaCl/metre^2 day)

The positive intercept on the wet-candle axis appears to be reasonable because the wet candle is continually collecting chloride on its moist surface while the rainfall can only collects those chloride particles which fall into the opening during a sedimentation process plus any chloride washed out of the air by rain. The wet candles stay relatively clean in a rural location and the determination of the chloride content of the solution is made easier by the absence of dirt. There was considerable variation between the results on individual samples because only a few milligrams of chloride are collected in a month and chloride-free conditions are difficult to maintain during handling. It is believed that about ten samples should be taken at each location and the sampling devices should be well dispersed on the sites. The analytical method could be improved but in order to have consistent results in this study the same method was used on both wet candle and rainfall can solutions.

The rainfall can is the easiest method of getting some indication of the chloride content of the air but it is very erratic in its sampling. It is not suited to arid conditions as rinsing a dry can with distilled water is difficult and gives unsatisfactory results. Rainfall cans freeze solid in sub-zero weather and they are of doubtful value when the precipitation is in the form of snow. The dirt and soot collected in urban locations makes the determination of chloride rather difficult.

York Redoubt is an exposed location on a cliff about 100 ft above the ocean and 300 ft back from the shore. Wet candle readings at this site appear to be influenced by strong wave action on the shore. Winds from the north, east and south could carry fine sea spray or dispersed sea salt past the wet candles. March 1959 was a very windy month with three periods of gale-force winds and twelve days of strong winds from seaward directions. These conditions are reflected in the very high chloride readings. Figure 6 is a hythergraph for the period covered by this report and it shows only one month when the prevailing wind direction was not favourable for carrying chloride over the site. This hythergraph was prepared from data supplied by the Halifax Weather Office and collected by its staff in Halifax and Dartmouth about seven and ten miles, respectively, from York Redoubt.

As can be seen from Fig. 2 there appears to be a systematic relation between the average rainfall and the amount of chloride collected at York Redoubt during a one month period. This is particularly noticeable when the chloride is measured by the rainfall can method. The correlation is shown in Fig. 7. This correlation appears to be absent in an urban location (Fig.3) where the chloride is probably related to the consumption of fuel and where inorganic and organic grime and soot interfere with the analysis for chloride. Neglecting the March 1959 reading, a line may be drawn through the remaining points by the method of least squares to give:

$$Y = 2.62X + 2.65$$

where

Y = chloride (mg NaCl/metre^2 day)

X = total precipitation (in.)

There appears to be little correlation between the chloride collected by the wet candles and the amount of rain. This is to be expected since the candles are kept under a roof and receive their chloride from the air which contacts them. The presence of soot and grime on the wet candles leads to low values for the chloride.

Some preliminary tests on the use of dry candles made of filter paper have been made but the amount of chloride collected was much smaller than with wet candles. These dry candles have all the desirable physical characteristics of the lead peroxide cylinders used for sulphur dioxide determinations and if the problems of reliable extraction and accurate analysis of the small amount of chloride which they collect can be solved they might be useful as a general method at all the outdoor exposure sites of the National Research Council.

Conclusions

1. Both wet candles and rainfall cans have serious limitations as general methods for the measurement of atmospheric chlorides under climatic conditions ranging from -60°F to 100°F and from high rainfall to arid.

2. It appears to be possible to relate the chloride as measured by the wet candle method to that determined from rainfall cans in the absence of appreciable amounts of dirt and soot.

3. The chloride content of the air in seaside locations appears to be more closely related to wave action and wind direction than to the total rainfall.

Reference

(1) Foran, M. R., E. V. Gibbons and J. R. Wellington. The measurement of atmospheric sulphur dioxide and chlorides. Chemistry in Canada, vol. 10, no. 5, May 1958, p.33-41; and reprinted as NRC 4758 by the National Research Council, Ottawa.

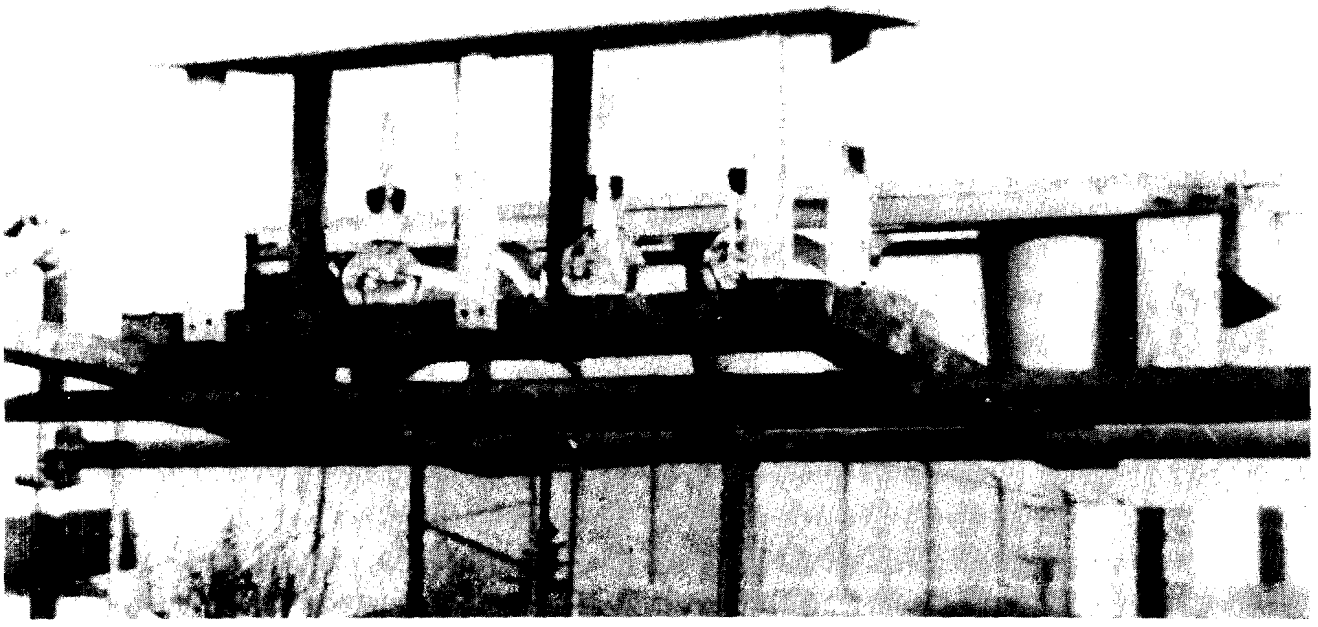

Figure 1 Arrangement of Rainfall Cans and Wet Candles at York Redoubt

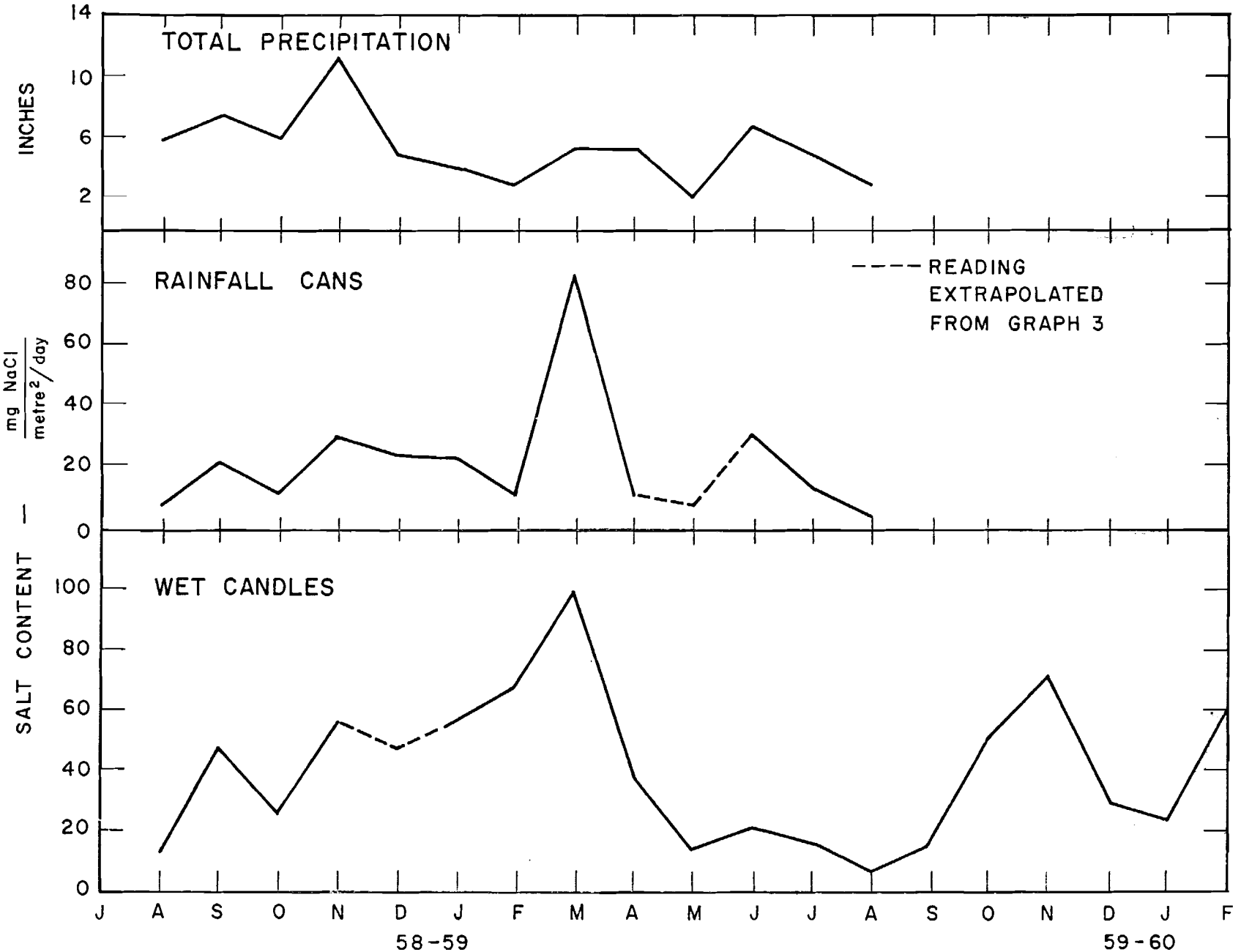

FIGURE 2 RESULTS AT YORK REDOUBT, N.S.

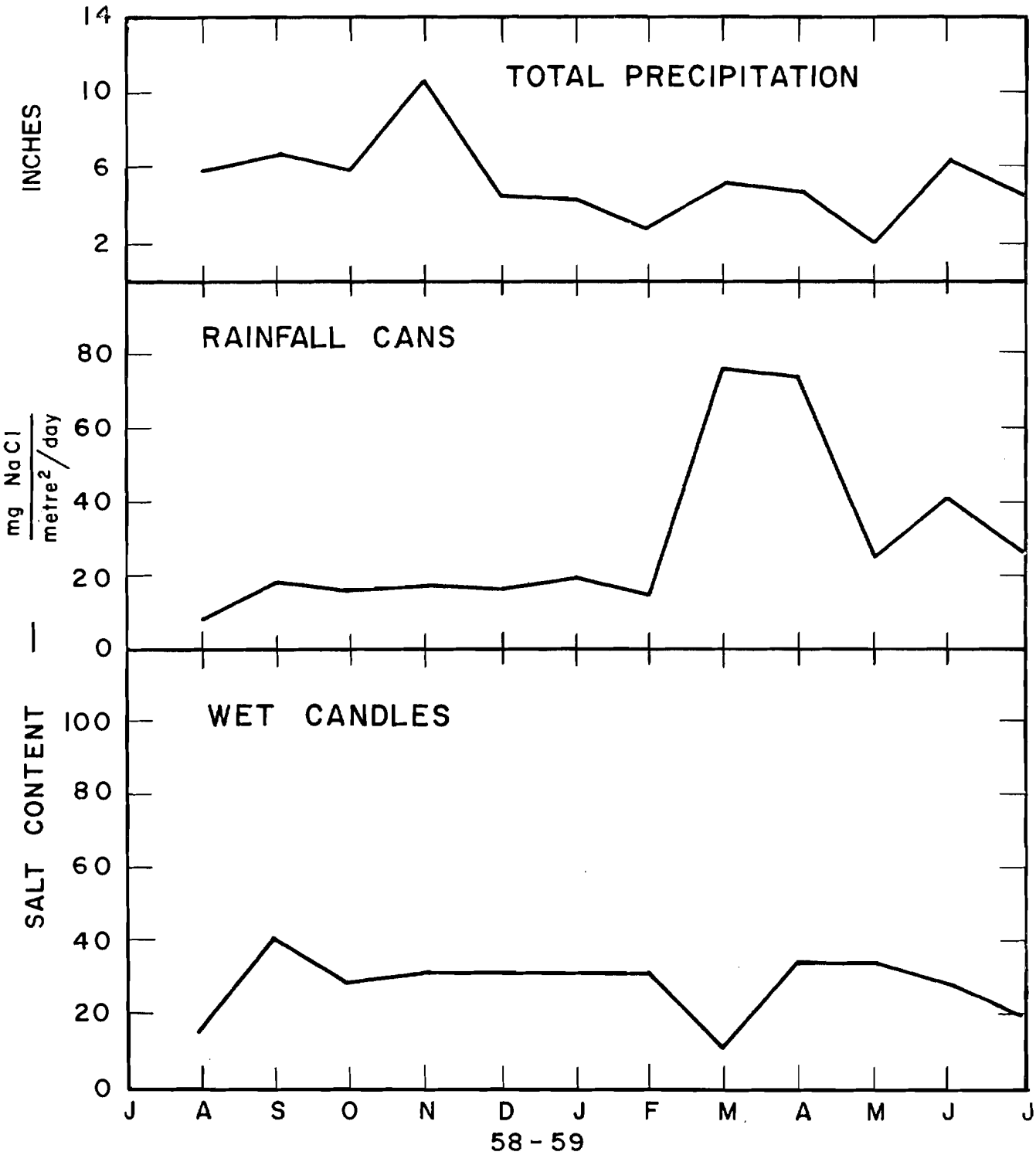

FIGURE 3
RESULTS AT THE NOVA SCOTIA TECHNICAL COLLEGE

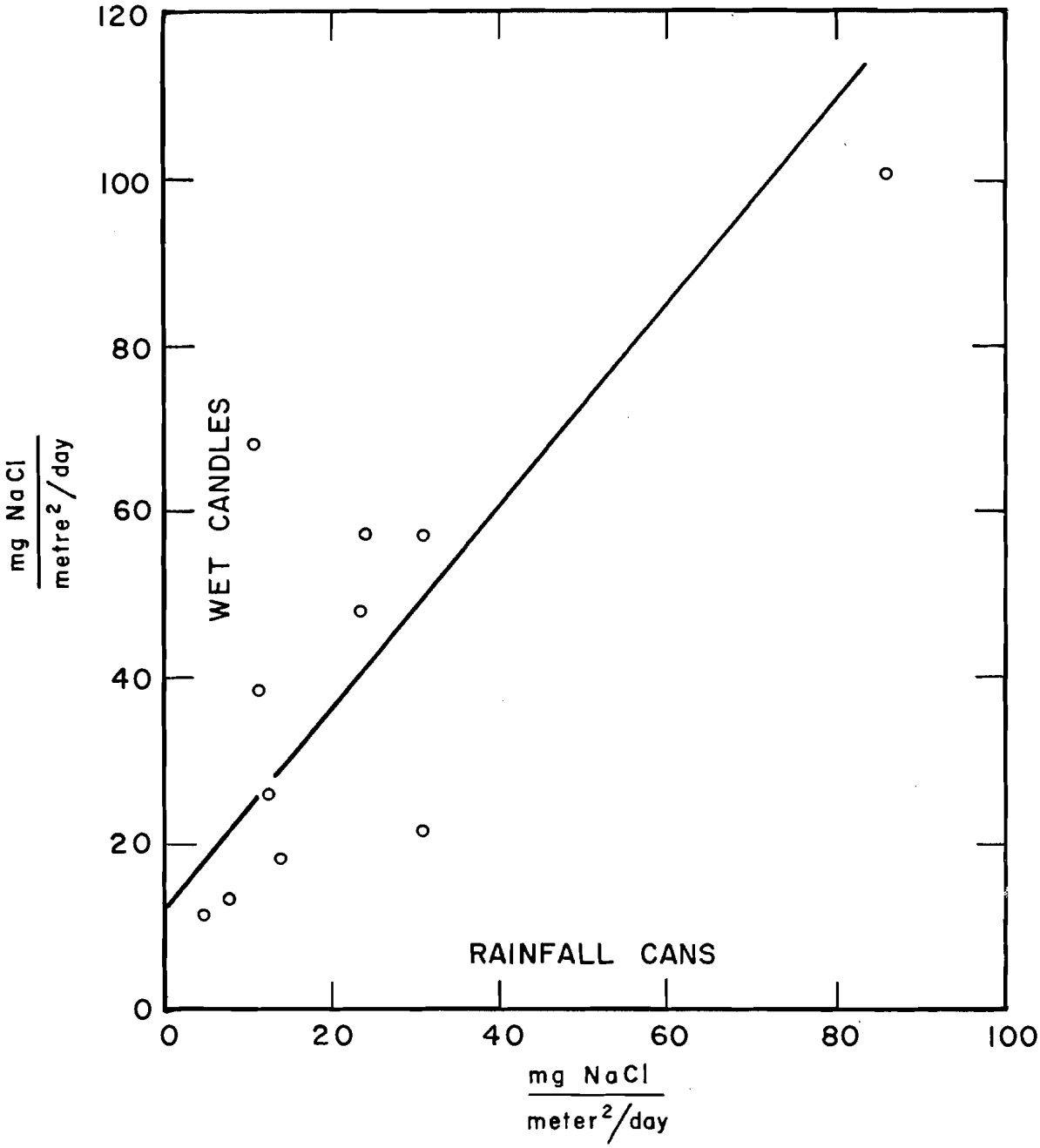

FIGURE 4
PLOT OF READINGS OBTAINED AT YORK REDOUBT, N.S.

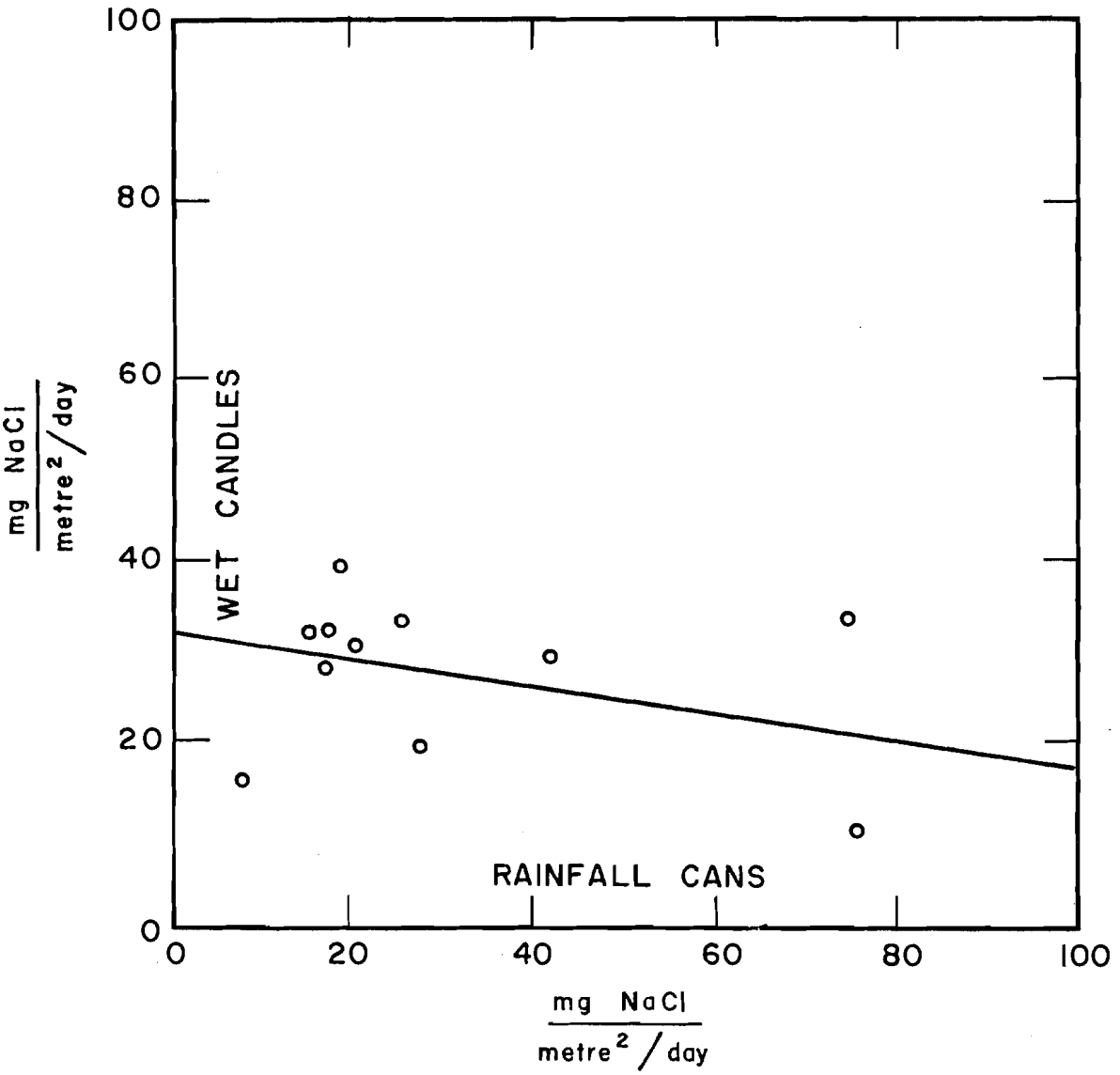

FIGURE 5
PLOT OF READINGS OBTAINED AT THE NOVA SCOTIA TECHNICAL COLLEGE

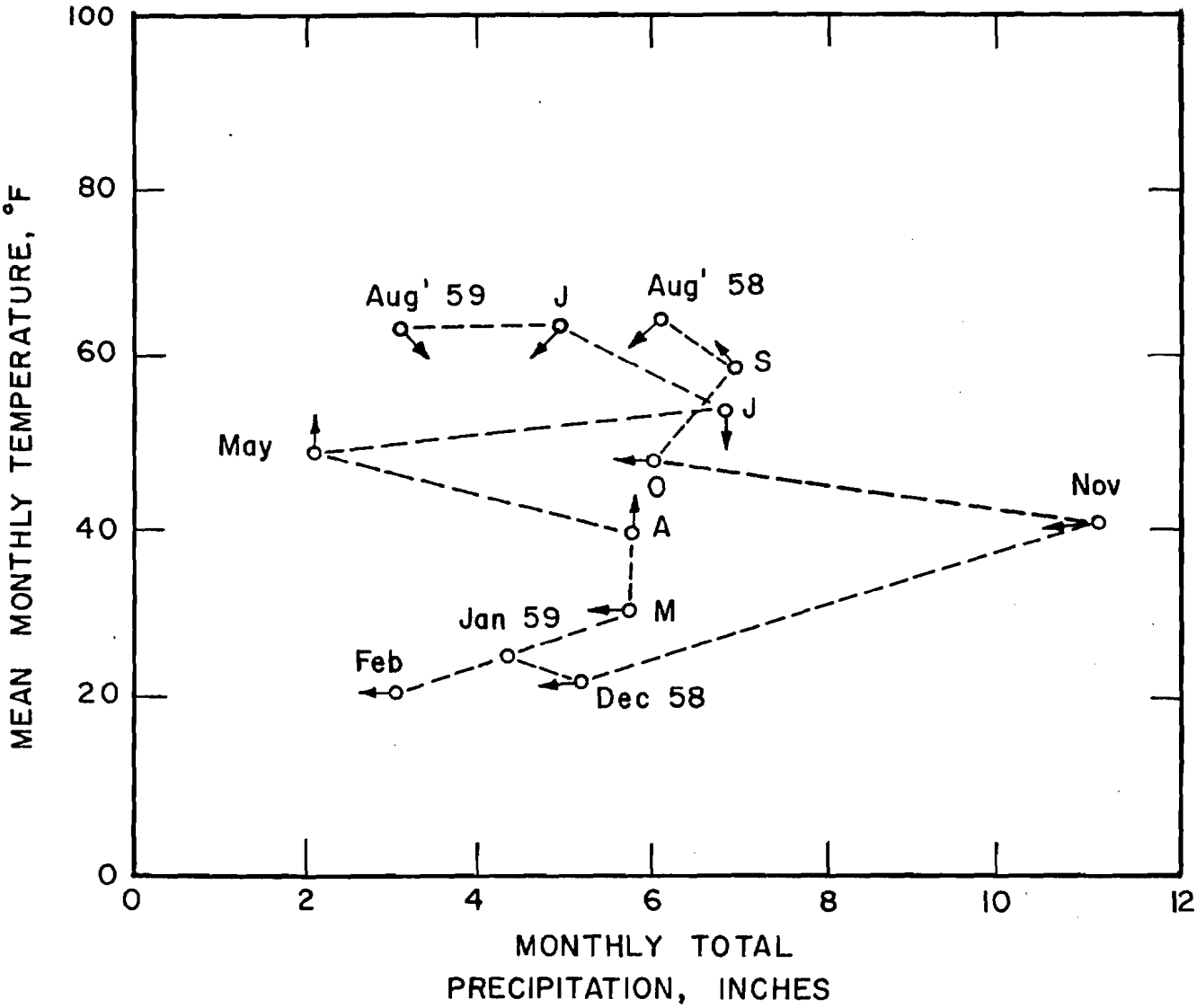

FIGURE 6
HYTHERGRAPH FOR HALIFAX

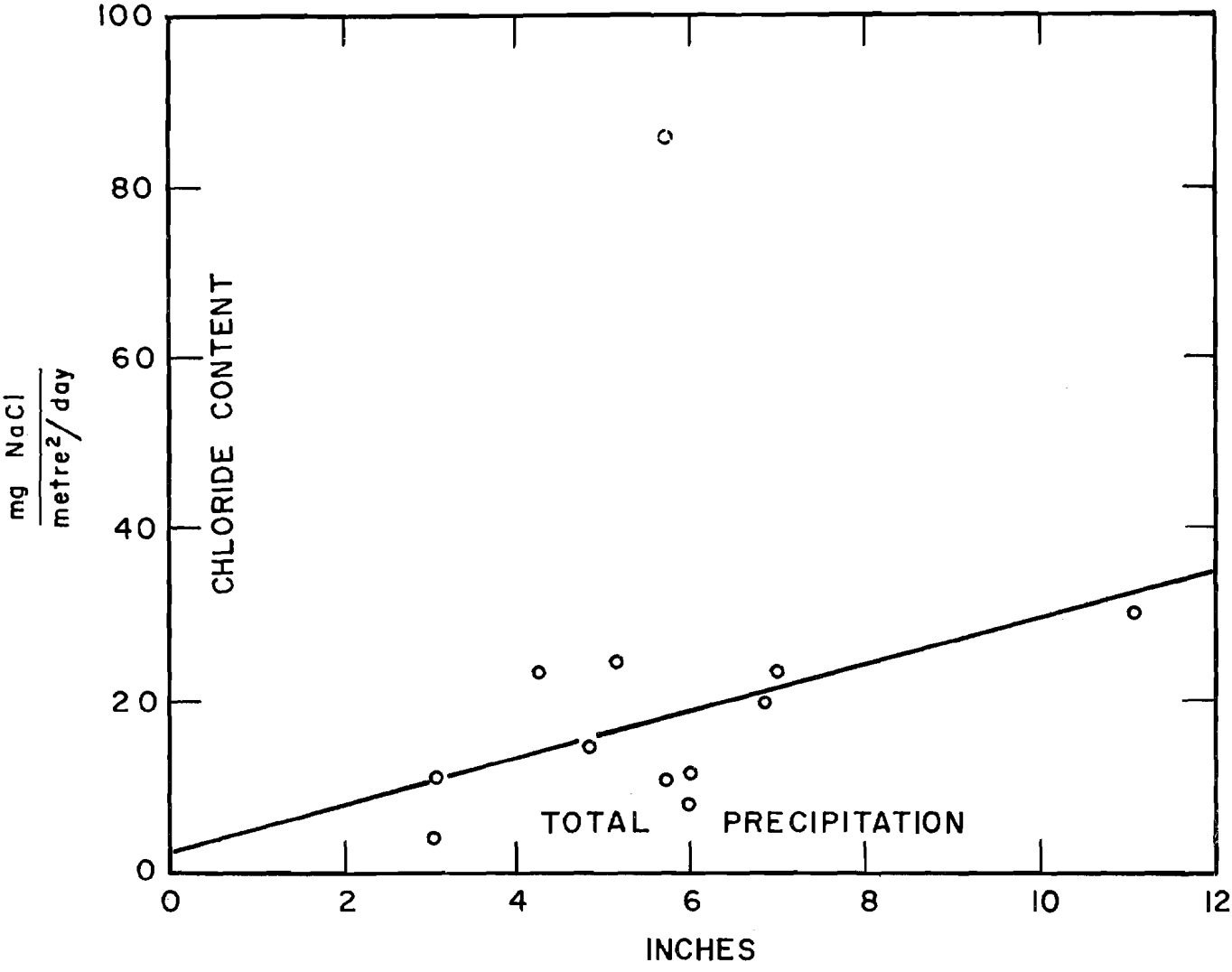

FIGURE 7
CORRELATION OF CHLORIDE BY RAINFALL CANS AND TOTAL PRECIPITATION